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Anionic surfactant biodegradation in seawater

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ABSTRACT

The authors conducted a study of the influence of several environmental factors (temperature, salinity, luminosity, aeration and the presence of sediments) on the biodegradation of a commercial anionic surfactant (LAS) in waters and sediments of Cadiz Bay (southwest Iberian Peninsula). The assay was carried out using an adaptation of the river die-away test. At temperatures of 20-25 °C, degradation exceeded 90 % within less than 10 days of assays, whereas at temperatures under 10 °C, degradation scarcely took place. Luminosity increases the degradation speed, compared with assays performed under darkness. Finally, the results show that the rate of surfactant degradation was remarkably accelerated in the presence of sediments, except in those tests where anoxic conditions were established.

Key words: Surfactant, LAS, seawater, biodegradation, sediments.

RESUMEN

Biodegradación de un tensioactivo aniónico en agua de mar

Se presenta un estudio de la influencia de diversas variables ambientales, tales como temperatura, salinidad, luminosidad, aireación, etc., en el proceso de biodegradación de un tensioactivo aniónico comercial (LAS) en aguas y sedimentos de la bahía de Cádiz (suroeste de la península Ibérica). El ensayo se ha llevado a cabo empleando una modificación del método test de agua de río. A temperaturas de 20 y 25 °C, el nivel de degradación superaba el 90 % en menos de 10 días de ensayo, mientras a temperaturas inferiores a los 10 °C, apenas tenía lugar degradación alguna. La iluminación provoca un aumento de la velocidad de degradación respecto a los ensayos llevados a cabo en oscuridad. Los resultados han mostrado que la velocidad de degradación del tensioactivo se ve claramente aumentada por la presencia de sedimentos, excepto en aquellos casos en los que se dieron condiciones anóxicas.

Palabras clave: *Tensioactivo, LAS, agua de mar, biodegradación, sedimentos.*

INTRODUCTION

Society's ever-expanding utilisation of materials, energy and space is accompanied by an increasing flux of anthropogenic organic chemicals into the environment. One of the several sets of transformations that remove organic compounds from the environment is that group of reactions mediated by organisms. As for chemical and photochemical reactions, these biochemical processes (biodegradation) change the structure of the organic chemical in question, thereby removing that particular compound from an environmental system of interest. The resulting one or more products (biointermediates) have their own properties, reactivities, fates and effects. It should be noted that when we refer to

biodegradation, we are not necessarily implying that they are fully mineralised. Mineralisation involves the complete degradation of an organic chemical to stable inorganic forms of C, H, N, P, and so on; consequently, complete mineralisation generally involves several successive biological transformations.

Although at a global level, soap is still the most widely-used surfactant product, the great variety of processes in which surfactants are involved has led to their extensive development (Granados, 1996).

Nearly 5 % of the 15 million t of surfactants consumed worldwide in 1995 was soap, and the rest were synthetic surfactants. Among these synthetic surfactants, LAS (figure 1) has the highest production rates. The volume of production in 1995 was approximately 1.5×10^6 t, which constitutes 18 % of total synthetic surfactant production (Granados, 1996).

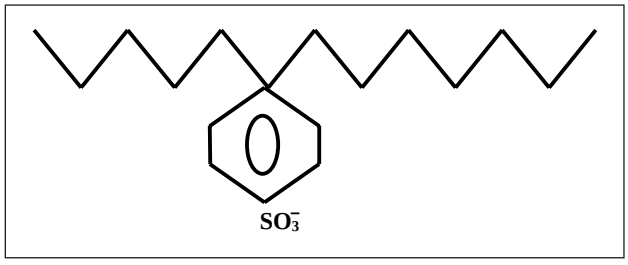

Figure 1. Sodium linear alkylbenzene sulphonate (LAS) structure

Hence, LAS constitutes a significant proportion of the xenobiotic compounds released into aquatic media (Hon-Nami and Hanya, 1980; Utsunomiya *et al.*, 1980). Therefore, over the last 30 years LAS has been the subject of numerous studies (e.g. Painter and Zabel, 1987), but few of them have been conducted in seawater (Vives-Rego *et al.*, 1987; Quiroga and Sales, 1990; Quiroga, Sales and Gómez-Parra, 1989) even though it is an important drainage destination of domestic wastewaters.

The aim of the present paper is to examine the impact of certain environmental factors on the process of LAS biodegradation in seawater, namely: temperature, salinity, luminosity, aeration, and the presence of sediments.

MATERIALS AND METHODS

The experiments were conducted using an adaptation of the river die-away test (Swisher, 1987). The surfactant studied was a commercial linear-chain sodium dodecylbenzene sulfonate (DBSNa), with 90.3 % active matter. All experiments were duplicated, and in all cases two samples were taken and analysed separately. The different values obtained from analysis showed a difference of < 5 %. The flasks were kept in thermostats with a temperature control accuracy of 0.1 °C. Immediately before each test, the surfactant was dissolved in sterilised water, then added to the flask. Total quantities of surfactant to be degraded at the start of each experiment are shown in table I, corresponding to the sum of the surfactant already contained in water and sediments plus the added surfactant. The quantities selected are similar to those found in the urban wastewater discharging into Cadiz Bay (Flores, Sales and Establier, 1980).

Analysis of the surfactant matter present in the medium at any time was performed using Abbot's Methylene Blue method (Abbot, 1962) (yield of a complex Methylene Blue-anionic surfactant, which can be extracted in chloroform). A full description of the degradation method employed and of the techniques for extracting surfactant from sludge has been published elsewhere (Sales *et al.*, 1984).

Dissolved oxygen (DO), pH and salinity of the seawater used in the tests were determined using the methods described by Strickland and Parsons (1968). Micro-organism counts were made according to Harrigan and McCance (1976). The characteristics determined in the sediments included organic C (Gaudette *et al.*, 1974), organic N (Anonymous, 1973), weight-loss at 110 °C and 450 °C, and various heavy metals (Fe, Mn, Zn, Cu, Pb, and Cd).

These were determined by atomic absorption spectroscopy after extraction from the sediment sample with HCl HNO3 (10:1) (Gómez-Parra, Establier and Blasco, 1984). Granulometric analysis was carried out by the chain hydrometer method.

The influence of temperature was studied with tests conducted with seawater only: 500 ml of water were put into a 1 000-ml flask for each of the working temperatures (5, 10, 15, 20 and 25 °C). During the experiments, the flasks were stoppered with hydrophobic cotton. The aliquots for determining residual surfactant concentration were collected with a pipette inserted to half the depth of the solution. Water samples for these tests were taken from point A (figure 2). The amount of surfactant added to each test and the characteristics of the

Table I. Physical-chemical characteristics and micro-organism counts of seawater samples used in tests. (1-5): temperature assays; (6-7): sediment assays; (8-11): salinity assays

Assay	Temperature (°C)	Salinity (‰)	pH	DO (mg/l)	Aerobic Micro-organisms (colonies/ml)	Surfactant initial amount (mg)
1-5	5-25	33.3	8.03	Saturation	1.71×10^4	0.48-0.53
6-7	20	33.8	8.10	7.61	8.00×10^3	2.00-2.50
8	25	16.06	8.12	9.78	4.20×10^3	1.74
9	25	32.2	8.11	6.50	8.50×10^3	1.71
10	25	49.9	8.13	2.71	1.28×10^4	1.66
11	25	65.1	8.14	1.50	1.69×10^4	1.80

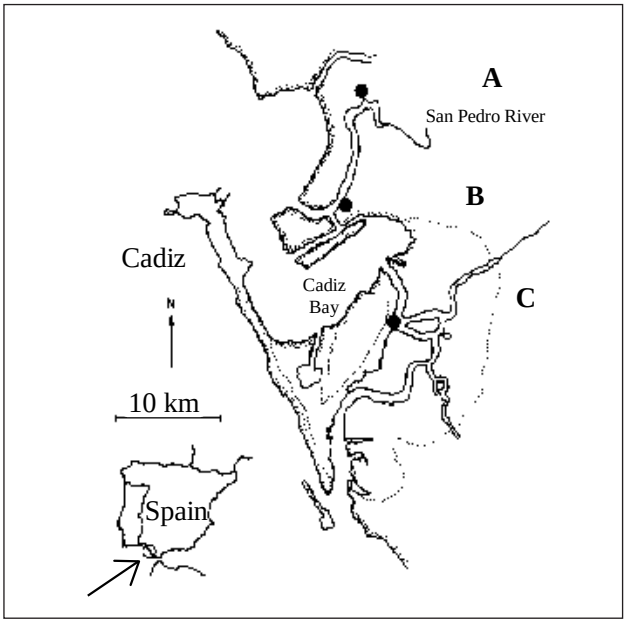

Figure 2. Location of water and sediment sampling points

Table II. Physico-chemical characteristics and micro-organism counts of sediment samples used in degradation tests

	Sediments A	B	C
Loss of weight 105 °C (%)	23.2	36.32	23.1
Loss of weight 450 °C (%)	9.76	13.48	4.9
Organic C (%) w/w dry	0.47	1.92	0.52
Organic N (%) w/w dry	0.04	0.25	0.03
Clay (%) w/w dry	26.6	56	68.7
Silt (%) w/w dry	28.4	30.2	10.3
Sand (%) w/w dry	45	13.8	21
Anionic Surfactant (µg LAS/g sed. dry)	4	28	3.3
Fe (%) w/w sed. dry	3.6	3.69	3.2
Mn (ppm) w/w sed. dry	518	342	375
Zn (ppm) w/w sed. dry	130	184	330
Cu (ppm) w/w sed. dry	20	47	13.7
Pb (ppm) w/w sed. dry	72	82	21.5
Cd (ppm) w/w sed. dry	1.36	2.47	2.17
Aerobic micro-organism (col./g) $\times 10^4$ (sed. wet)]	10	20	24
Anaerobic micro-organism (col./g) $\times 10^4$ (sed. wet)]	6	7.2	2.3

seawater employed are shown in the first row of table I.

For the tests in the presence of sediments, a separate solution was used for each determination. In these cases, 250-ml flasks were used, with 100 ml of water and 25 g of sediment wet weight. This ratio of water volume and sediment weight is similar to that used by other authors to study processes of transference of heavy metals and nutrients through the water-sediment interface (Van Kessel, 1978). The influence of sediments on the degradation process was tested with samples of sediments from points A and B (figure 2). The characteristics of the sediment samples used are shown in table II. The amount of surfactant added to each test and the characteristics of the seawater employed are shown in the second row of table I.

For the tests carried out at different salinities, the experimental procedure was similar to that of the tests conducted to study sediment influence. Seawater was used from a salt-pond located at point C (figure 1) which had undergone severe evaporation (S = 65 ‰). Other salinities at which surfactant degradation was studied (50, 32 and 16 ‰) were obtained by dilution with sterile distilled water. These tests were conducted in the presence of sediments taken at location A. The amount of surfactant added to each test and the characteristics of the seawater employed are shown in the third to sixth rows of table I.

To test the influence of light, samples were subjected to a constant luminosity of 1 254 lux, with visible light. Aeration was studied by keeping the flask closed while an aerator introduced filtered, purified air at 1 l/min. The effect of darkness was

tested by leaving the samples in a totally dark room for the entire duration of the assay. The water used for the assays of aeration and luminosity (S= 32 ‰) was also obtained by diluting water from point C (S = 62 ‰) and the sediments were taken from point C, as well (figure 2).

RESULTS AND DISCUSSION

Influence of temperature on degradation

Table III shows percentages of degradation reached on different days of testing, for the five temperatures studied. Generally speaking, it can be seen that there was hardly any degradation at low temperatures (5-10 °C), while at 25 °C, more than 90 % of the surfactant had disappeared 15 days after the start of the experiment. At intermediate temperatures, only a small amount of degradation took place.

The dependence on temperature of the rate at which the degradation process occurs is related to the metabolism of the micro-organisms responsible for degradation. Therefore, the pollution potential of urban waste containing surfactants undergoes marked seasonal variations. In coastal areas where water temperature ranges from 5-10 °C (frequent winter temperatures in the study area), the adverse effects of discharging anionic surfactant products will be considerably enhanced, due to their longer presence in the medium. This is particularly important in coastal areas with little water renewal where any kind of aquaculture is carried out, since a large number of marine species spawn during the winter, and their larvae and alevins are especially sensitive to surfactants.

Biodegradation in the presence of sediments

Figure 3 shows the results of the test conducted with sediments. For the sake of reference, it includes the variation of the percentage of degradation with time, in a test using water without sediment. All of these experiments were run at 20 °C. It could be seen that in both cases, because of the presence of sediment, the degradation rate is very high, with only a few days of assay. This means that the period of acclimatisation of the bacterial flora was substantially shortened.

However, the two types of sediment behaved very differently. With type A, 90 % degradation was reached before day 10 of the test. With type B, although there was rapid degradation at the outset, from day 6 to 7 on, it scarcely occurred. The discrepancies must lie in the differences between the two types of sediments used, both in terms of their physical nature and the degree of pollution at their place of origin.

The granulometry of the A-type sediments shows an important sand component and consequently a low organic matter content. The B-types, on the other hand, show a predominance of clay, with a substantial amount of organic matter. As regards their degree of contamination, type A comes from a channel running into the Bay of Cadiz, with a low contamination level, whereas type B was taken about 500 m from the main wastewater outlet for the city of San Fernando (100 000 inhabitants). There, the concentration of heavy metals is very high and the water layers close to the sediment are in reduced conditions.

The oxidising conditions at the start of the tests (7.61 mg 0_2/l) encouraged bacterial action on a large number of organic compounds easily biodegradable in such conditions and present in appreciable concentrations in the sediments from area B (compounds with high organic N content). This degradation occurs at the same time as that of the added surfactant. The high benthic demands on the oxidation of organic substances in the sedi-

Table III. Percentage degradation reached on different days of testing in experiments conducted at different temperatures

	Time (days)													
Temperature (°C)	1	2	3	4	5	6	7	8	9	10	11	13	15	21
5	0.9	1.1	1.3	1.5	1.7	1.8	2.0	2.0	2.4	2.6	3.1	3.4	3.6	4.2
10	0.3	1.7	2.1	4.2	7.5	9.0	11.5	13.3	14.0	15.0	20.0	28.6	33.1	36.0
15	2.3	4.2	5.8	9.4	13.4	17.5	22.2	25.0	27.5	30.2	37.1	42.6	44.8	47.9
20	1.1	2.5	5.2	6.3	8.7	11.3	15.5	17.3	20.6	24.2	29.2	40.5	48.3	69.7
25	1.7	3.7	6.5	9.9	14.3	20.0	26.4	38.5	41.0	48.8	62.7	87.0	92.7	97.0

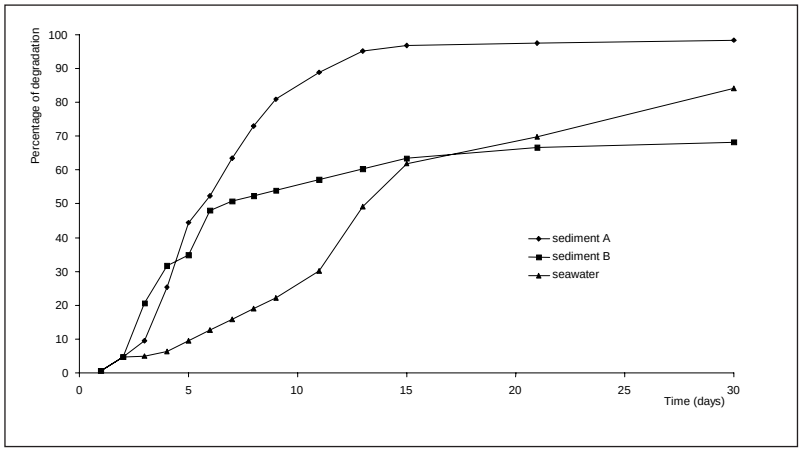

Figure 3. Variation of percentage degradation with time at 20 °C

ment exhausted the available oxygen in a few days. From that moment on, surfactant degradation had to take place through anaerobic pathways, which must be carried out by the micro-organisms present. These are generally less efficient than aerobic processes, as is proven by the finding that there was only appreciable degradation of surfactants with B-type sediment while there was enough dissolved oxygen in the supernatant water to sustain aerobic bacterial activity.

In addition, during the experiments with these sediments there could have been some inhibition of bacterial growth due to the toxicity of some of the heavy metals that were present in very high concentration (Pb, Cu). There are two decisive factors affecting the toxicity of heavy metals: the direction in which the transfer of metals takes place between the sediment and the interstitial water, and their speciation when in solution (Forstner and Wittmann, 1979), both conditioned by the redox potential value. Hence, if the physico-chemical conditions in the medium became modified in the course of the biodegradation experiments, this could induce the appearance of bacteriostatic substances.

Influence of variation in the medium's salinity

In the case of the assays at varying salinities (figure 4), it can be seen that, similarly, there are no significant differences in the levels reached after 21 days. The difference lies in the induction period, which is shorter for high salinities (65 and 50 ‰) than for lower ones (32 and 16 ‰). This may be because degrading bacteria are halophilous, accustomed to existence in very saline media, so that dilution would result in the disappearance of large numbers of them; then again, those remaining would require a longer period to adapt to the new medium. The reason for the lack of differences in percentage degradation reached at the end of 21 days for the various salinities studied, must be

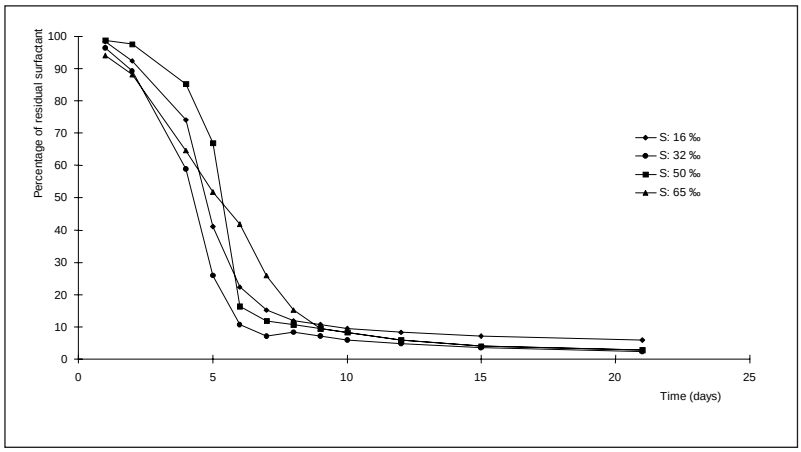

Figure 4. Change with time of percentage of residual surfactant for different salinity assays

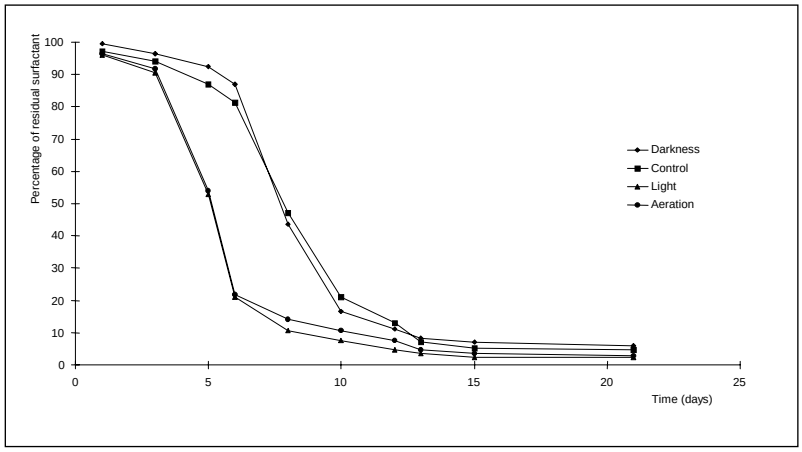

Figure 5. Change with time of percentage of residual surfactant as influenced by aeration, luminosity and darkness

sought in the presence of sludge in the medium used for the degradation assays.

Influence of aeration and luminosity

Figure 5 shows that although there are no significant differences in percentage degradation reached over the entire 21 days of experimentation, the aerated and illuminated samples attained 90 % degradation in roughly 4 days less than the other cases. To explain the higher degradation speed in the aeration assays, it should be considered that degradation is basically an aerobic process, and hence the introduction of air to the solution will favour it.

In the luminosity assays, increased speed can probably be explained by photosynthetic activity in the micro-algae present in the seawater. Artificial light was used in these experiments, but from a spectrum very close to that of sunlight. There is further reason to believe that light in the presence of photosynthesisers may affect the degradation process.

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